

INCLUSION OF NITROGEN AT THE SILICON DIOXIDE-SILICON CARBIDE INTERFACE FOR PASSIVATION OF INTERFACE DEFECTS

This application claims the benefit under 35 U.S.C. § 119 (e) of United States Provisional Application No. 60/192,009, filed March 24, 2000, which is incorporated herein by reference in its entirety.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

This invention was made with government support under grant # MDA972 98-1-0007 awarded by the Defense Advanced Research Projects Agency (DARPA). The federal government has certain rights in the present invention.

BACKGROUND OF THE INVENTION

1. FIELD OF THE INVENTION

The present invention relates to silicon carbide semiconductor devices and methods for their construction. More specifically, the instant invention relates to silicon carbide semiconductor devices with a layer of silicon dioxide disposed on a silicon carbide substrate that have a region of substantial nitrogen concentration at the silicon dioxide-silicon carbide interface.

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2. DESCRIPTION OF THE RELATED ART

Presently, the silicon (Si) metal-oxide-semiconductor field effect transistor (MOSFET) is the most commonly manufactured transistor in the world. Silicon carbide (SiC) MOSFETs are currently being developed because of superior material properties that provide high power generation, conditioning, transmission and the ability to operate at higher temperatures.

Like Si, SiC thermally oxidizes to form SiO₂. However, the oxidation kinetics and oxide interface of SiC are poorly understood in comparison to Si. The oxidation rate of SiC is lower than Si by more than a factor of 10. Furthermore, the quality of the SiO₂/SiC interface is also inferior to the SiO₂/Si interface. This problem causes

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interface. In one embodiment, the silicon carbide substrate is 4H-SiC. In another embodiment, the silicon carbide substrate is 6H-SiC. In yet another embodiment, the silicon carbide substrate is doped with a p-type or n-type dopant.

5 The silicon dioxide layer is formed by cleaning and then oxidizing the silicon carbide substrate. Preferably, the silicon carbide substrate is cleaned with 10% HF and then thermally oxidized. In a preferred embodiment, the silicon carbide substrate is oxidized at between about 900 °C and about 1200 °C. Preferably, the silicon dioxide layer is greater than about 10 Å thick.

10 In one embodiment, nitrogen is incorporated by annealing the semiconductor device in nitric oxide or nitrous oxide. Preferably, in this embodiment, the semiconductor device is annealed at between about 950 °C and about 1200 °C (more preferably, at about 1175 °C) for between about 1 and about 4 hours. In another embodiment, nitrogen is incorporated by annealing the semiconductor device in ammonia at about between 950 °C and about 1200 °C (more preferably, at about 1175 °C) for about 4 hours.

15 Preferably, the areal density of nitrogen at the silicon dioxide/silicon carbide interface is between about $0.5 \times 10^{14} \text{ cm}^{-2}$ and about $1 \times 10^{16} \text{ cm}^{-2}$ (more preferably, between about $1 \times 10^{14} \text{ cm}^{-2}$ and about $2 \times 10^{15} \text{ cm}^{-2}$). In a preferred embodiment, the maximum concentration of nitrogen at the silicon dioxide/ silicon carbide interface is about 0.5%.

20 In another aspect, the present invention provides a silicon carbide semiconductor device. The semiconductor device has a silicon carbide substrate with a layer of silicon dioxide disposed thereon. The silicon dioxide/silicon carbide interface is characterized by a region of substantial nitrogen concentration.

25 In one embodiment, the silicon carbide substrate is 4H-SiC. In another embodiment, the silicon carbide substrate is 6H-SiC. In yet another embodiment, the silicon carbide substrate is doped with a p-type or a n-type dopant. Preferably, the areal density of nitrogen at the silicon dioxide/silicon carbide interface is between about $0.5 \times 10^{14} \text{ cm}^{-2}$ and about $1 \times 10^{16} \text{ cm}^{-2}$ (more preferably, between about $1 \times 10^{14} \text{ cm}^{-2}$ and about $2 \times 10^{15} \text{ cm}^{-2}$).

In one preferred embodiment, the maximum concentration of nitrogen at the silicon dioxide/ silicon carbide interface is about 0.5%. In another preferred embodiment, the layer of silicon dioxide is greater than about 10 Å thick.

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BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 schematically illustrates a SiO₂/SiC semiconductor device of the current invention.

Figure 2 is an excitation curve of the nuclear reaction of ¹⁵N(p,α) ¹²C (E_R =
10 429 keV) for SiO₂/SiC annealed in 10 mbar of ¹⁵N¹⁸O at 1000°C for 4 h. The dots are the experimental data and the lines are the simulated excitation curves, components and sum, assuming the ¹⁵N profiles shown in Figure 4.

Figure 3 is an excitation curve of the nuclear reaction of ¹⁸O(p,α) ¹⁵N (E_R=151
15 keV) for SiO₂/SiC annealed in 10 mbar of ¹⁵N¹⁸O at 1000°C for 4 h. The dots are the experimental data and the lines are the simulated excitation curves, components and sum, assuming the ¹⁸O profiles shown in Figures 6.

Figure 4 is the concentration profile of ¹⁵N in SiO₂/SiC annealed in 10 mbar of
20 ¹⁵N¹⁸O at 1000°C for 1 h (dotted) and 4 h (solid). The origin corresponds to the surface and the SiO₂/SiC interface is at about 30 nm.

Figure 5 is the concentration profile of ¹⁵N in SiO₂/Si annealed in 10 mbar of
25 ¹⁵N¹⁸O at 1000°C for 1 h (dotted) and 4 h (solid). The origin corresponds to the surface and the SiO₂/Si interface is at about 20 nm.

Figure 6 is a concentration profile of ¹⁸O in SiO₂/SiC annealed in 10mbar of
¹⁵N¹⁸O at 1000°C for 1 h (dotted) and 4 h (solid). The origin corresponds to the surface and the ¹⁸O gradient is due to the surface exchange reaction.

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Figure 7 is a concentration profile of ^{18}O in SiO_2/Si annealed in 10mbar of $^{15}\text{N}^{18}\text{O}$ at 1000 °C for 1 h (dotted) and 4 h (solid). The origin corresponds to the surface and the ^{18}O gradient is due to the surface exchange reaction.

Figure 8 illustrates the electrical effects of passivation techniques for $\text{SiO}_2/6\text{H-SiC}$ and $\text{SiO}_2/4\text{H-SiC}$ samples annealed in NO for about two hours at about 1100 °C. Similar results are achieved with NH_3 .

DETAILED DESCRIPTION OF THE INVENTION

Reference will now be made in detail to preferred embodiments of the invention. While the invention will be described in conjunction with the preferred embodiments, it will be understood that it is not intended to limit the invention to those preferred embodiments. To the contrary, it is intended to cover alternatives, modifications, and equivalents as may be included within the spirit and scope of the invention as defined by the appended claims.

Figure 1 schematically illustrates a semiconductor device of the current invention. Semiconductor device 112 has a silicon dioxide layer 110 disposed on silicon carbide substrate 102. Silicon dioxide layer 110 consists of two different regions 106 and 108. Region 108, which is located at the SiO_2/SiC interface 104, is a region of substantial nitrogen concentration. The nitrogen concentration of region 106 is substantially lower than the nitrogen concentration of region 108.

Preferably, silicon dioxide layer 110 is greater than about 200 Å thick. Preferably, region 106 is between about 200 Å thick and about 1000 Å thick (more preferably, between about 300 Å thick and about 500 Å thick) Preferably, region 108 is between about 10 Å thick and about 30 Å thick (more preferably, between about 20 Å thick and about 30 Å thick).

The silicon carbide substrate 102 is 4H-SiC or 6H-SiC (preferably, 4H-SiC) and may be doped with either a p-type or a n-type dopant. The silicon carbide substrate 102 may also include an epitaxial layer. Preferably, the areal density of nitrogen at the silicon dioxide/silicon carbide interface 104 is between about $0.5 \times 10^{14} \text{ cm}^{-2}$ and about $1 \times 10^{16} \text{ cm}^{-2}$ (more preferably, between about $1 \times 10^{14} \text{ cm}^{-2}$ and about $2 \times 10^{15} \text{ cm}^{-2}$). The nitrogen concentration at the silicon dioxide/ silicon carbide

interface is between about $10^{22}/\text{cm}^3$ and about $10^{20}/\text{cm}^3$. The maximum concentration of nitrogen at the silicon dioxide/ silicon carbide interface is about 0.5%.

The semiconductor device shown in Figure 1 may be made by methods well known to those of ordinary skill in the art. For example, silicon dioxide may be deposited on a silicon carbide substrate by conventional deposition methods. The device may then be annealed with a nitrogen containing gas to provide a region of high nitrogen concentration such as area 108 at the SiO_2/SiC interface 104.

The silicon carbide substrate is 4H-SiC or 6H-SiC (preferably, 4H-SiC) and may be doped with either a p-type or a n-type dopant. The layer of silicon dioxide is preferably formed by cleaning the silicon carbide substrate followed by oxidation of the silicon carbide substrate. Preferred cleaning procedures include standard organic, heavy metals and RCA cleaning methods. Preferably, the silicon carbide substrate is cleaned with 10% HF. In a preferred embodiment, the silicon carbide substrate is thermally oxidized using standard wet or dry techniques. Preferably, the silicon carbide substrate is oxidized at between about 900 °C and about 1200 °C (more preferably, between about 1050 °C and about 1200 °C).

Nitrogen may be incorporated at the silicon carbide silicon dioxide interface by annealing in the presence of a nitrogen containing gas. Preferably, the nitrogen containing gas is nitric oxide, nitrous oxide or ammonia. When the nitrogen containing gas is nitric oxide, nitrous oxide or ammonia, the semiconductor device is annealed at between about 950 °C and about 1200 °C (more preferably, between about 1050 °C and about 1200 °C, (most preferably, at about 1175 °C)) for between about 1 and about 4 hours.

Preferably, the areal density of nitrogen at the silicon dioxide/silicon carbide interface 104 is between about $0.5 \times 10^{14} \text{ cm}^{-2}$ and about $1 \times 10^{16} \text{ cm}^{-2}$ (more preferably, between about $1 \times 10^{14} \text{ cm}^{-2}$ and about $2 \times 10^{15} \text{ cm}^{-2}$). The nitrogen concentration at the silicon dioxide/ silicon carbide interface is between about $10^{20}/\text{cm}^3$ and about $10^{22}/\text{cm}^3$. The maximum concentration of nitrogen at the silicon dioxide/ silicon carbide interface is about 0.5%.

EXAMPLES

The invention having been described, the following examples are presented to illustrate, rather than limit, the scope of the invention. The examples illustrate various embodiments and features of the present invention.

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EXAMPLE 1: PREPARATION OF ANNEALED 4H-SiC WAFERS

Preparation of silicon-faced (8° off axis) 4H-SiC wafers with a p-type substrate and epitaxial layer, doped at about $2 \times 10^{16} \text{ cm}^{-3}$ and n-type (100) Si wafers with a resistivity of about $10 \Omega\text{-cm}$ required etching in a 10% HF solution to remove native
10 oxide and thermal oxidation in a resistively heated quartz tube furnace. The 4H-SiC wafers were oxidized in wet oxygen (oxygen bubbled through deionized water at about $85\text{-}90^\circ\text{C}$) at a flow rate of about 1.0 l/mm. The 4H-SiC wafers were then loaded in a wet oxidizing ambient at about 850°C , the temperature was raised to about 1150°C and the samples were oxidized for about 30 minutes in accordance with prior art
15 techniques. The ambient was then switched to argon, the temperature was lowered to about 800°C and the SiC wafers were removed from the furnace. The oxide thickness for the SiC wafers was about 30 nm.

When annealing was carried out with ^{15}N containing gases the following conditions were typically employed. The 4H-SiC wafers were annealed in a resistively
20 heated quartz tube furnace in 99.7% $^{15}\text{N}^{18}\text{O}$ or $^{15}\text{N}_2\text{O}$ at a static pressure of about 10 mbar at about 1000°C for either about 1 or about 4 hours. Alternatively, the 4H-SiC wafers were annealed in 99.7% $^{15}\text{NH}_3$ at a static pressure of about 10 mbar at about 1100°C for about 4 hours.

However, when annealing was carried out with ^{14}N containing gases different
25 conditions were typically employed. Annealing was preferably carried out at gas flow rates of about 0.5 l/min at atmospheric pressure and at temperatures between about 1000°C and about 1200°C for between about one and about six hours.

EXAMPLE 2: PREPARATION OF ANNEALED 4H-Si WAFERS

30 Si wafers were oxidized in dry oxygen ($<2\text{ppm H}_2\text{O}$) at a flow rate of about 1 l/min, loaded in a oxidizing ambient at about 900°C and oxidized at about 900°C

for about 25 minutes. The ambient was then switched to argon, and the Si wafers were removed from the furnace. The oxide thickness for Si wafers was about 20 nm.

The Si wafers were then annealed in a resistively heated quartz tube furnace with 99.7% $^{15}\text{N}^{18}\text{O}$ or $^{15}\text{N}_2\text{O}$ at a static pressure of about 10 mbar at about 1000 °C for either about 1 or about 4 hours. When annealing was carried out with ^{14}N containing gases the conditions specified above were typically used. Anneals were preferably carried out at gas flow rates of about 0.5 l/min at atmospheric pressure, at temperatures between about 1000 °C and about 1200 °C for between about one and about six hours.

10 EXAMPLE 3: MEASUREMENT OF AREAL DENSITIES

The areal densities of ^{15}N and ^{18}O of annealed Si/C and Si wafers prepared as described in Examples 1 and 2 were determined by Nuclear Reaction Analysis (NRA) using the reactions $^{15}\text{N}(\text{p},\alpha\gamma)^{12}\text{C}$ at $E_p=1$ MeV and $^{18}\text{O}(\text{p},\alpha\gamma)^{15}\text{N}$ at $E_p=730$ keV. The ^{15}N and ^{18}O depth profiles were determined by nuclear resonance profiling (NRP) using the resonances in the reactions $^{15}\text{N}(\text{p},\alpha\gamma)^{12}\text{C}$ at 429 keV and $^{18}\text{O}(\text{p},\alpha)^{15}\text{N}$ at 151 keV, respectively, and a tilted sample geometry ($\psi=65^\circ$). The measured excitation curves (γ or α yield versus incident proton energy) around the resonance energy were converted into concentration versus depth profiles. Table 1, shown below summarizes oxidation conditions, anneal times, oxide thickness and areal densities for a number of experiments.

Table 1.

Material	Oxidation Conditions	$^{15}\text{N}^{18}\text{O}$ Anneal Time (hours)	^{15}N Areal Density (10^{15} cm^{-2})	^{18}O Areal Density (10^{15} cm^{-2})	Oxide Thickness (nm)
Si	900°C-Dry	1	1.6	19.6	20.3
Si	900°C-Dry	4	2.2	44.6	22.8
SiC	1150°C-Wet	1	0.1	15.9	28.9
SiC	1150°C-Wet	4	0.2	51.0	27.6

An excitation curve and its simulation for the $^{15}\text{N}(\text{p},\alpha\gamma)^{12}\text{C}$ reaction in a SiO_2/SiC sample annealed in $^{15}\text{N}^{18}\text{O}$ are shown in Figure 2. The obtained depth

profiles of ^{15}N in the SiO_2/SiC samples (Figure 4) are similar to the profiles in the SiO_2/Si samples (Figure 5). Nitrogen is concentrated primarily at the SiO_2/SiC interface at about 30 nm. The width of the N profile is larger in the SiO_2/SiC samples than in the SiO_2/Si samples, which suggests that the SiO_2/SiC interface is rougher than the SiO_2/Si interface. These depth profiles, determined by nuclear resonance profiling, provide independent verification of SIMS results, which showed nitrogen located near the interface.

- The ^{15}N areal density in SiO_2/SiC wafers is about 10^{14} cm^{-2} for both anneal times (see Table 1), and the maximum nitrogen concentration is about 0.5 % (see Figure 4) when the wafers are annealed in $^{15}\text{N}^{18}\text{O}$. Both of these values are much smaller than SiO_2/Si wafers, where the ^{15}N areal density is about 10^{15} cm^{-2} and the maximum concentration is about 10%. The rate of nitrogen incorporation in both SiO_2/SiC and SiO_2/Si wafers is related to their relative oxidation rates, which suggests that the rate of Si-N bonding at the interface is governed by the same factors as the oxidation rate in each material.

- An excitation curve and its simulation for the $^{18}\text{O}(\text{p},\alpha)^{15}\text{N}$ reaction in a SiO_2/SiC wafer annealed in $^{15}\text{N}^{18}\text{O}$ are shown in Figure 3. The ^{18}O depth distributions in the SiO_2/SiC wafers (Figure 6) show a gradient of ^{18}O in the oxide from the surface to the interface. These ^{18}O profiles, as well as the ^{18}O areal densities (see Table 1), strongly resemble those of the Si wafers (Figure 7). In Si wafers however, ^{18}O accumulates at the interface, while little or no new oxidation occurs in SiC wafers. These results confirm the difference in oxidation rates of SiC and Si and indicate that the surface exchange mechanism is identical for oxides on SiC and Si. Since the exchange reaction is solely a characteristic of the oxide and not the substrate, this was further evidence of similar chemical behavior of oxide on SiC and Si substrates.

- In SiO_2/SiC wafers annealed in $^{15}\text{N}_2\text{O}$, the amount of nitrogen incorporated is about 10^{13} cm^{-2} , which is near the detection limit of NRA and prevents resonance profiling. The amount of incorporated nitrogen is again an order of magnitude smaller than the amount of nitrogen in the SiO_2/Si samples, which is about 10^{14} cm^{-2} .

- The above results are particularly meaningful when the electrical properties of oxynitrides on SiC are considered. Previous studies showed that thermal annealing of $\text{SiO}_2/6\text{H-SiC}$ in NO at 1100°C modestly decreased the interface trap density (D_{it}),

while N_2O anneal actually increased D_{it} . In contrast, the present invention demonstrates that rapid thermal annealing of $SiO_2/4H-SiC$ in NO at $1100^\circ C$ significantly decreases the interface trap density (D_{it}).

- A small but definite incorporation of nitrogen near the SiO_2/SiC interface from NO anneal and considerably less nitrogen incorporation from N_2O anneal is observed (see Figures 2-7). Thermal decomposition of NO at temperatures $>1000^\circ K$ provides a fairly constant concentration of NO along with small amounts of N_2 and O_2 . Conversely, N_2O readily decomposes into N_2 (about 60%), O_2 (about 25%), and NO (about 15%). The dominant reaction when oxide films are annealed in N_2O is dry oxidation of the substrate. Annealing in N_2O incorporates very little nitrogen at the interface because of the low NO concentration and leads to poor quality, dry oxidation of SiC, which provides a high interface trap density. The re-oxidation technique (annealing SiO_2/SiC , in wet oxygen at $950^\circ C$) improves interface quality without appreciable new oxide growth by reducing D_{it} near the middle of the band gap.
- 15 Nitrogen incorporation at the $SiO_2/4H-SiC$ interface may offer benefits similar to the re-oxidation anneal, by substantially reducing D_{it} near the conduction band edge, which also could explain the different results in NO and N_2O anneals.

- Thus, annealing SiO_2/SiC wafers in N_2O incorporates less nitrogen (about $10^{13} cm^{-2}$) while annealing in NO incorporates nitrogen near the SiO_2/SiC interface with an areal density of about $10^{14} cm^{-2}$ and an atomic concentration of about 0.5%.
- 20 Annealing in NH_3 provides reductions in D_{it} similar to those that are achieved using NO; however, NH_3 annealing incorporates nitrogen in the SiO_2 layer with a much higher areal density (about $10^{16} cm^{-2}$).

- Compared to SiO_2/Si , nitrogen incorporation is lower for $SiO_2/4H-SiC$ annealed in NO but higher for $SiO_2/4H-SiC$ annealed in NH_3 . These values are an order of magnitude lower than comparably prepared SiO_2/Si wafers. Like SiO_2/Si , a surface exchange of oxygen in the gas phase with the oxide followed by NO diffusion and reaction at the SiO_2/SiC interface are observed after NO anneal. The surface exchange reaction for SiO_2/SiC appears to be similar to SiO_2/Si confirming that the oxides themselves are chemically similar. The incorporation of nitrogen at the interface provides a possible explanation for the electrical characteristics of NO, NH_3 , and N_2O annealed $SiO_2/4H-SiC$ wafers. In particular, the interface trap density near
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the conduction band in $\text{SiO}_2/\text{4H-SiC}$ wafers is substantially reduced after high temperature annealing in either NO and NH_3 . These results suggest that any process that incorporates atomic nitrogen at the SiO_2/SiC interface may reduce the interface trap density in $\text{SiO}_2/\text{4H-SiC}$ wafers. The process described above facilitates

- 5 improvements in the channel mobility for inversion mode, n-channel MOSFETS, fabricated with 4H-SiC.

EXAMPLE 4: COMPARISON OF ANNEALING OF $\text{SiO}_2/\text{6H-SiC}$ AND $\text{SiO}_2/\text{4H-SiC}$ WAFERS

- 10 Figure 8 illustrates the effect of annealing $\text{SiO}_2/\text{6H-SiC}$ and $\text{SiO}_2/\text{4H-SiC}$ samples in nitric oxide (NO) and hence serves to show the electrical effects of the passivation techniques of the current invention. Similar results are observed using ammonia (NH_3) instead of NO . A reduction in the interface state density near the conduction band edge of approximately one order of magnitude is observed for the
- 15 $\text{SiO}_2/\text{4H-SiC}$ sample compared to the $\text{SiO}_2/\text{6H-SiC}$ sample. This experimental observation is in agreement with prior art suggestions that indicate a large interface state density exists for all polytypes of SiC at around 2.9eV above the valence band edge. In 6H-SiC, these states lie mostly in the conduction band and hence are not affected by passivation techniques. However, 4H-SiC, the material of choice for SiC
- 20 MOSFET fabrication, has a wider band gap than 6H-SiC (~3.3eV compared to ~3eV), and as a result, a much larger fraction of the interface states near 2.9eV lie in the band gap of 4H-SiC where they act to degrade channel mobility for n-channel, inversion mode devices through field termination, carrier (electron) trapping and Coulomb scattering. Therefore, the current invention, as shown in Figure 8, by identifying
- 25 passivation techniques for these states, significantly improves prospects for SiC MOSFET manufacture.

- Finally, it should be noted that there are alternative ways of implementing both the process and apparatus of the present invention. For example, the silicon carbide semiconductor substrate may be annealed at different temperature, pressures or even
- 30 with different nitrogen containing gases. The silicon carbide semiconductor device may contain regions of higher or lower nitrogen concentration at the silicon carbide/silicon dioxide interface than described in the present invention. Accordingly,

the present embodiments are to be considered as illustrative and not restrictive, and the invention is not to be limited to the details given herein, but may be modified within the scope and equivalents of the appended claims.

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